

# Giant Thermomechanical Effect in Normal Liquid $^3\text{He}$

D.L. Sawkey, D. Deptuck, D. Greenwood, and J.P. Harrison\*

*Physics Department, Queen's University, Kingston, Ontario K7L 3N6, Canada*  
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Measurements are presented of the thermomechanical coefficient of normal liquid  $^3\text{He}$  confined in a porous plug pre-plated with four monolayers of  $^4\text{He}$ . These nonmagnetic monolayers displace the magnetic solid-like  $^3\text{He}$  monolayers that are adjacent to the pore surfaces when the plug is filled with pure  $^3\text{He}$ . In the low temperature limit ( $T \leq 10$  mK) the coefficient can be described by  $\Delta P/\Delta T \sim s/6v$  where  $\Delta P$  is the pressure difference across the plug generated by the temperature difference  $\Delta T$  and  $s$  and  $v$  are the molar entropy and molar volume. This low temperature limit corresponds to the condition  $d \ll \ell_q$  where  $d$  is the pore diameter and  $\ell_q$  is the bulk liquid  $^3\text{He}$  quasiparticle mean free path; that is, the quasiparticles are predominantly boundary scattered in the pores. The measured coefficient is half that calculated by Edwards, Culman and He. When compared with this new experimental result for the  $^4\text{He}$ -plated porous plug, the earlier result for pure liquid  $^3\text{He}$  is strikingly larger (by up to  $30\times$  at 2 mK). This enhancement is reminiscent of the giant thermopowers measured in Kondo and other dilute magnetic alloys. It is speculated that the enhanced thermomechanical coefficient for pure liquid  $^3\text{He}$  is due to magnetic scattering of the  $^3\text{He}$  quasiparticles by the two magnetic solid-like  $^3\text{He}$  monolayers adjacent to the pore surfaces.

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## I. INTRODUCTION

An earlier paper presented results for a new thermomechanical effect, in normal liquid  $^3\text{He}$  confined within the nanoscale pores of a porous plug [1]. This was seen as the liquid  $^3\text{He}$  Fermi liquid analogue of thermoelectricity, the classical gas thermomolecular effect, and the phonon thermomechanical effect [2] in a general liquid. There is also the analogy with the superfluid  $^4\text{He}$  thermomechanical effect, except that this is a reversible effect [3] (no entropy production or flow) whereas the others need to be described by irreversible thermodynamics [4,5]. The thermomechanical effect in normal liquid  $^3\text{He}$  required boundary scattering of the  $^3\text{He}$  quasiparticles just as the thermomolecular effect in a classical gas and the phonon thermomechanical effect need an orifice or tube with diameter less than the molecular and phonon mean free paths, respectively.

The measurement itself was of  $\Delta P/\Delta T$  where  $\Delta T$  was the temperature difference across the plug and  $\Delta P$  was the resulting pressure difference.<sup>†</sup> The temperature difference was established by a heat current through the  $^3\text{He}$  confined within the pores of the plug and measured with a cerous magnesium nitrate thermometer, calibrated against a  $^3\text{He}$  melting-curve thermometer [6].

The pressure was measured absolutely in terms of the head of liquid  $^3\text{He}$  in a liquid  $^3\text{He}$  manometer. The thermomechanical coefficient  $\Delta P/\Delta T$  was substantial,  $\sim 10$  kPa/K or  $\sim 10$  mm  $^3\text{He}/\text{mK}$  over the temperature range 2–25 mK.

A separate experiment showed that the thermomechanical coefficient was zero for an open geometry, a tube with diameter  $D \gg \ell_q$ , where  $\ell_q$  is the  $^3\text{He}$  quasiparticle mean free path for scattering by other quasiparticles. This is also the case for the classical gas thermomolecular effect in the hydrodynamic limit  $D \gg \lambda$ , where  $\lambda$  is the molecular mean free path [4]. The measured liquid  $^3\text{He}$  coefficient with the confined  $^3\text{He}$  was therefore some weighted average of the boundary scattering coefficient and the zero coefficient due to scattering by other quasiparticles. A Nordheim-Gorter [7] procedure, familiar in the field of thermoelectricity, was used to extract the coefficient due to boundary scattering alone. This correction was important for  $T \geq 10$  mK where  $\ell_q \leq d$  and  $d$  is the pore diameter.

The introduction continues with two sections which describe a comparison of the measured coefficient with a theoretical calculation and a review of some surface effects that could account for the resulting disagreement.

## A. Theory

The first theoretical approaches to thermoelectricity in a metal and the thermomolecular effect in a gas were based upon equilibrium thermodynamics (see, for example, the monograph by Denbigh [5]). Consider the case of two chambers containing a classical gas connected by

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<sup>†</sup>Historically,  $\Delta P/\Delta T$  was called the thermomolecular effect for the classical gas and the thermomechanical effect for superfluid  $^4\text{He}$ . We have chosen to use the term thermomechanical effect because we are studying liquid helium, although in the normal state.

a small orifice; chambers 1 and 2 are at temperatures  $T$  and  $T + \Delta T$  and pressures  $P$  and  $P + \Delta P$ . In dynamic equilibrium the effusion rates from 1 to 2 and from 2 to 1 are the same. Elementary thermodynamics and kinetic theory then lead to  $\Delta P/\Delta T = -q^*/vT$  and  $q^* = -cT/3$ , respectively, where  $q^*$ ,  $v$  and  $c$  are the molar heat of transport, molar volume, and constant volume molar specific heat respectively. The heat of transport is a flow of heat from hot to cold, while in dynamic equilibrium, and hence is a continuing source of entropy. The process is therefore irreversible and irreversible thermodynamics must be used.

The linear transport laws within irreversible thermodynamics can be written in terms of generalized currents and forces as  $J_i = \sum_k L_{ik} X_k$  where  $L_{ik}$  is a transport coefficient and  $J_i$ ,  $X_i$  are chosen so that  $\sum_i J_i X_i = dS/dt$ , the rate of entropy production [4]. Onsager [8] used the principle of microscopic reversibility to show that  $L_{ij} = L_{ji}$ . In our case, the driving forces for the liquid  $^3\text{He}$  quasiparticles arise from the differences of chemical potential,  $\mu$ , and of temperature across the porous plug. With quasiparticle molar flow rate  $J_N = dN/dt$  and energy flow rate  $J_U = dU/dt$ , Onsager's equations become

$$J_N = -L_{11}\Delta\left(\frac{\mu}{T}\right) + L_{12}\Delta\left(\frac{1}{T}\right) \quad (1)$$

$$J_U = -L_{21}\Delta\left(\frac{\mu}{T}\right) + L_{22}\Delta\left(\frac{1}{T}\right) \quad (2)$$

or, using standard thermodynamics identities,

$$J_N = -\frac{L_{11}v}{T}\Delta P + \frac{L_{11}h - L_{12}}{T^2}\Delta T \quad (3)$$

$$J_U = -\frac{L_{21}v}{T}\Delta P + \frac{L_{21}h - L_{22}}{T^2}\Delta T \quad (4)$$

where  $h$  is the molar enthalpy. The thermomechanical coefficient results from the condition  $J_N = 0$ , so that

$$\frac{\Delta P}{\Delta T} = \frac{h - (L_{12}/L_{11})}{vT} \quad (5)$$

As an aside, the condition  $\Delta T = 0$  gives

$$J_U = \frac{L_{21}}{L_{11}}J_N \equiv u^*J_N \quad (6)$$

where  $u^*$  is the molar energy of the transport. Therefore, equation (5) becomes

$$\frac{\Delta P}{\Delta T} = \frac{h - u^*}{vT} \equiv -\frac{q^*}{vT} \quad (7)$$

where  $q^* = u^* - h$  is the heat of transport. Thus, the reversible thermodynamics result is retrieved. To go further, one needs a microscopic model for the system of interest, for example kinetic theory for the classical gas.

Following the formalism used by Smith in his review [9] for transport in a Fermi liquid, Edwards, Culman and He [10] developed the particle current and energy current transport equations for simultaneous pressure and temperature gradients. Both cylindrical geometry and a mesoscopic structure described in terms of the Landauer-Buttiker formalism were considered. In both cases Edwards et al. found

$$\frac{\Delta P}{\Delta T} = \frac{s}{3v} = \frac{C_v}{3} \quad (8)$$

where  $s$  and  $v$  are the molar entropy and molar volume, and  $C_v$  is the constant volume heat capacity per unit volume. The second equality results from the linear temperature dependence of the heat capacity. The positive sign signifies a flow of  $^3\text{He}$  from cold to hot in establishing the pressure difference. Note that  $C_v/3$  is identical to the thermomolecular coefficient in a classical gas and  $s/3v$  is 1/3 the thermomechanical effect in a superfluid.

Compared to the theoretical result, the measured coefficient was larger by  $15\times$  at 2 mK and  $3\times$  at 20 mK, although the sign was correct. Disagreements of this size, and larger, are well known in thermoelectricity [11]. In general they are associated with energy dependent scattering by Kondo and other magnetic impurities [12].

## B. Boundary Scattering of $^3\text{He}$ Quasiparticles

For liquid  $^3\text{He}$ , the obvious source of magnetic scattering is the magnetic solid-like layer of  $^3\text{He}$  atoms adjacent to the  $^3\text{He}$ -copper oxide interface within the porous plug; another possibility<sup>‡</sup> is the magnetism of the copper oxide itself [13]. A Curie-law component in the magnetism of confined liquid  $^3\text{He}$  was first found for  $^3\text{He}$  in vycor glass [14]. Curie-Weiss behaviour was demonstrated a few years later for  $^3\text{He}$  confined between mylar sheets [15]. The magnetism was clearly identified with  $^3\text{He}$  adjacent to the interface by pre-plating the mylar with two monolayers of  $^4\text{He}$  atoms and finding that the Curie-Weiss term was absent. The  $^4\text{He}$  atoms are preferentially attracted to the interface [16,17]; although the van der Waals force of attraction to the interface is identical for  $^3\text{He}$  and  $^4\text{He}$ , the larger mass of the  $^4\text{He}$  atom leads to a lower ground state energy and consequently a larger binding energy. The first two monolayers adjacent to the interface are bound with high density and are solid-like whereas the third and higher monolayers are part of the bulk liquid. Therefore the pre-plating of two or more monolayers of  $^4\text{He}$  leaves all of the  $^3\text{He}$  as liquid with the small Pauli paramagnetism of a Fermi liquid.

By now there is a fairly clear picture of the  $^3\text{He}$  interface magnetism [18–20] and, to a lesser extent, of the

<sup>‡</sup>Julian Brown, private communication.

scattering of  $^3\text{He}$  quasiparticles at the boundary either with pure  $^3\text{He}$  or with  $^4\text{He}$  pre-plating [21–24]. For pure  $^3\text{He}$  on very flat carbon (Grafoil) substrates the first monolayer has solid-like density and is a Curie-law paramagnet. The binding to the underlying substrate is sufficiently strong that there is no significant exchange within the monolayer. The second monolayer is less dense, but still solid-like. It is a Curie-Weiss paramagnet with Weiss constant  $\theta \sim -0.5$  mK (antiferromagnetic). The magnetism of the second monolayer is independent of whether the first monolayer is  $^3\text{He}$  or  $^4\text{He}$ , suggesting that the second layer exchange is intra-layer. As this second monolayer is overlaid with more  $^3\text{He}$ ,  $\theta$  rapidly switches from  $\sim -0.5$  mK to  $\sim +0.5$  mK (ferromagnetic), although whether this is caused by interlayer exchange or density enhancement of the second monolayer is not known. Bozler et al. [25] have shown evidence of ferromagnetic order of the solid-like  $^3\text{He}$  below 1 mK by measuring the magnetization in a very small applied field. On other substrates such as mylar [15,22], fluorocarbon beads [26], sintered silver powder [27], and aerogel [28] (a silica structure with up to 99% porosity) there is also Curie-Weiss paramagnetism with  $\theta \sim +0.5$  mK, although specific heat measurements [29,30] suggest that a wide range of  $\theta$  values is required to explain the results. In all cases where the substrates have been pre-plated with two or more monolayers of  $^4\text{He}$ , the surface magnetism has been eliminated [15,22,27,28].

Evidence for the nature of the scattering of  $^3\text{He}$  quasiparticles at the interface, whether pure  $^3\text{He}$  with its surface magnetism or  $^4\text{He}$  pre-plated, has come from a variety of experiments: the drag force on moving  $^3\text{He}$ , the boundary value of the superfluid order parameter,  $^3\text{He}$  spin relaxation and energy exchange across the interface (Kapitza conductance). Viscous slip at the boundary is an important correction to measurements of viscosity [31]. It can be described by a specularity constant  $\nu$ , the fraction of quasiparticles that are specularly scattered at the boundary; the rest are diffusely scattered [9]. This is a concept that goes back to Maxwell [32]. Specularity enhances flow through a tube by a factor  $(1+\nu)/(1-\nu)$ . Ritchie et al. [21] measured the temperature dependent response of a Stycast epoxy torsional oscillator filled with  $^3\text{He}$  and found a decrease in the real and imaginary components of the transverse surface impedance when  $\sim 2$  or more  $^4\text{He}$  monolayers were pre-plated onto the epoxy, clear evidence for increased specularity. However, they were unable to fit their results with a theoretical model. Freeman and Richardson [22], working with a torsional oscillator with a mylar surface, found similar behaviour and specularities consistent with the range 0.75–0.9 with  $^4\text{He}$  monolayers present. Tholen and Parpia [33] similarly measured a jump in  $\nu$  from 0.4 to 0.9 when two  $^4\text{He}$  monolayers were added to a silicon torsional oscillator.

Freeman and Richardson [22] and Steel et al. [24] studied superfluidity in thin films of  $^3\text{He}$ , on mylar and copper substrates respectively. Both groups found suppression of the transition temperature for pure  $^3\text{He}$ ; the suppression

was consistent with zero order parameter at the interface, as expected for diffuse scattering of the  $^3\text{He}$  quasiparticles. Surprisingly at the time, the two groups found no suppression of the transition temperature when the mylar or copper substrates were pre-plated with  $\sim 2$  monolayers of  $^4\text{He}$ , suggesting that the  $^4\text{He}$ -plated interface was acting as a mirror surface for the  $^3\text{He}$  quasiparticles. Kim et al. [23] found similar behaviour from fourth sound measurements on  $^3\text{He}$  confined in a packed powder: suppression of the superfluid density with pure  $^3\text{He}$  and a relative increase when the pores were pre-plated with  $^4\text{He}$ . Ritchie et al. and Freeman and Richardson have emphasized the dilemma of these results: The surfaces are not atomically flat and will not be made so by the addition of just two monolayers of  $^4\text{He}$ . Therefore, geometrically diffuse scattering is to be expected for both  $^3\text{He}$  and  $^4\text{He}$  at the interface.

Other experiments have addressed the question of magnetic spin flip and energy exchange at the boundary. In general the low temperature relaxation of magnetization in liquid  $^3\text{He}$  is determined by relaxation at the boundary. This was demonstrated by Kelly and Richardson [34], Hammel and Richardson [26], and Godfrin et al. [35] among others. In particular, by writing  $T_1 = d/\epsilon\nu_F$ , where  $T_1$  is the spin relaxation time,  $d$  is the characteristic size of the pores and  $\epsilon$  is the spin-flip probability at the boundary [36], Godfrin et al. found  $\epsilon \sim 10^{-6}$  for  $^3\text{He}$  confined in the pores of platinum powder and  $\epsilon \sim 10^{-8}$  in alumina powder and Grafoil. These values of  $\epsilon$  were reduced by a factor  $\sim 100$  when the substrates were pre-plated with 2.7 monolayers of  $^4\text{He}$ ; a similar observation had been made by Kelly and Richardson. In contrast with these very low probabilities for spin flip, NMR measurements of  $^3\text{He}$  in confined geometries show just one absorption line [37,27,28]. The frequency is a weighted average of the solid and liquid  $^3\text{He}$  frequencies and reflects the rapid exchange of  $^3\text{He}$  atoms between the liquid  $^3\text{He}$  and solid surface  $^3\text{He}$  atoms.

The probability for energy exchange by a  $^3\text{He}$  quasiparticle can be deduced from the Kapitza thermal boundary resistance [38,39]. In his review Harrison concluded that a lower limit had been reached at  $RT \sim 300$  K<sup>2</sup>/W for 1 cm<sup>3</sup> of sintered metal powder heat exchanger. This can be re-expressed as  $\dot{Q}/TV\Delta T \sim 3 \times 10^3$  W m<sup>-3</sup> K<sup>-2</sup> where  $\dot{Q}/\Delta T$  is the boundary conductance and  $V$  is the volume of the heat exchanger. A theoretical model [40] for the heat exchange gave the result  $\dot{Q}/TV\Delta T \sim 4 \times 10^{-15}/d^3$  W m<sup>-3</sup> K<sup>-2</sup> which was shown to give a reasonable representation of the experimental results [41]. This result translates into a probability  $\epsilon'$  for thermal energy transfer by a quasiparticle at the boundary of  $\epsilon' \sim 10^{-10}$  for 1  $\mu\text{m}$  pores and  $\epsilon' \sim 10^{-8}$  for 0.1  $\mu\text{m}$  pores.

The conclusions to be drawn from the experiments are that for pure  $^3\text{He}$  there is a Curie-Weiss surface magnetism which is eliminated by pre-plating the substrate with two or more  $^4\text{He}$  monolayers. The pure  $^3\text{He}$  surface scatters the  $^3\text{He}$  quasiparticles largely diffusely but

with a very small probability of spin-flip or energy exchange. Without the surface magnetism the  $^3\text{He}$  quasiparticles are scattered specularly, or largely specularly, and the probability of spin-flip or energy exchange is reduced even further. Following Freeman and Richardson [22], since two monolayers cannot flatten a rough surface, the surfaces must be atomically flat, at least over a length scale comparable to the de Broglie wavelength of the  $^3\text{He}$  quasiparticles ( $2\pi/k_F \sim 1 \text{ nm}$ ). Therefore the diffuse scattering at the magnetic surface must be magnetic in origin, but not, in general, accompanied by spin-flip or energy exchange. Sprague et al. [28] have considered a magnetic scattering model based upon the scattering of quasiparticles by a field induced magnetic polarization of the surface  $^3\text{He}$  atoms, but a general calculation is still required.

In view of the above discussion, it is clear that the important test for attributing enhancement of the thermomechanical effect to diffusive magnetic scattering at the interface is to pre-plate the porous plug with two or more monolayers of  $^4\text{He}$  atoms. A reason for expecting that this would have an effect goes back to the original observation [24] that led us to the thermomechanical effect in liquid  $^3\text{He}$ : During adiabatic demagnetizations of the  $\text{PrNi}_5$  nuclear cooling refrigerator there was evidence for movement of  $^3\text{He}$  in runs with pure  $^3\text{He}$  but not in 24 of the 27 runs with  $^4\text{He}$  pre-plating.

This paper presents the results of pre-plating the porous plug with four monolayers of  $^4\text{He}$ . Section 2 presents a summary of the experiment. Section 3 is a presentation and discussion of the results, and conclusions are drawn in Section 4. A brief description of the results has been presented at the 1997 Symposium on Quantum Fluids and Solids [42].

## II. THE EXPERIMENT

The apparatus and experiment have been described elsewhere [1]. For completeness, a schematic diagram and brief description are included here. The U-tube geometry of the  $^3\text{He}$  manometer is shown in Fig. 1. The bottom of the U-tube was open to the  $\sim 10 \text{ cm}^3$  reservoir of liquid  $^3\text{He}$  in the heat exchanger attached to the adiabatic demagnetization refrigerator. The left-hand arm or tower contained a thin film heater, thermally isolated from the apparatus by thin superconducting leads, and a cerous magnesium nitrate magnetic thermometer. It also contained the porous plug which separated the  $^3\text{He}$  into two regions, ideally at temperatures  $T + \Delta T$  above the plug (with added heat) and  $T$  below the plug. In practice, there were temperature gradients within the  $^3\text{He}$  and, as described below, corrections had to be made. The right-hand tower was a coaxial capacitor level detector, partially filled with liquid  $^3\text{He}$  also at temperature  $T$ . Once the apparatus had been filled with liquid  $^3\text{He}$  and equilibrium established, pressure differences across

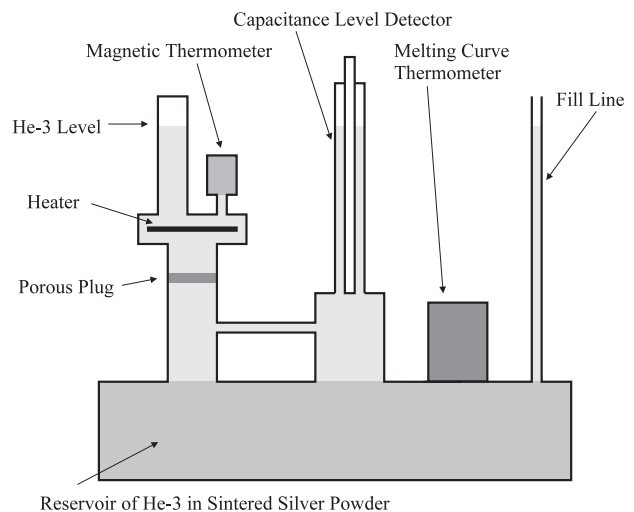


FIG. 1. A schematic illustration of the apparatus. The left-hand tower and the capacitance level detector, together with the cross-over tube, form a liquid  $^3\text{He}$  manometer. The  $^3\text{He}$  chamber is connected below to the adiabatic demagnetization refrigerator and above, via a superconductor heat switch, to a dilution refrigerator.

the plug were indicated by level changes in the coaxial capacitor. Short term (minutes) and long term (hours) sensitivities of 1 and  $5 \mu\text{m}$  were realizable. The level detector was calibrated by measuring the empty and full capacitance values and measuring separately the length of the capacitor.

The porous plug was packed 70 nm oxidized copper powder, 6.3 mm diameter by 1.3 mm height. The packing fraction was  $0.35 \pm 0.03$  by volume. Oxidized copper was used so that the thermal conductance of the plug would be negligible compared to that of the liquid  $^3\text{He}$  in the pores. The mechanical time constant for  $^3\text{He}$  flow through the porous plug, and hence of the manometer, was long and the consequent 1–2 days required for each data point was an obvious disadvantage compared to a diaphragm pressure transducer [43]; however, the level detector does have the advantage of giving an absolute measure of the pressure difference.

A separate tower above the main heat exchanger chamber contained a  $^3\text{He}$  melting curve thermometer; this was used to monitor the temperature of the  $^3\text{He}$  below the porous plug and, with no added heat, to calibrate the magnetic thermometer.

The experiment proceeded as follows: The  $^4\text{He}$  for the pre-plating, equivalent to four monolayers, was admitted to the  $^3\text{He}$  space at liquid nitrogen temperature and given time at that temperature and also at 4 K and 1 K to distribute itself uniformly over the  $\sim 50 \text{ m}^2$  surface. The melting curve thermometer was filled at 1 K and the  $^3\text{He}$  space partially filled (see Fig. 1) at  $\sim 0.5 \text{ K}$  where the  $^3\text{He}$  viscosity is a minimum. The lower stage was cooled to below 1 mK and gradually warmed to calibrate the melting curve thermometer against the superfluid  $^3\text{He}$

A-transition and to calibrate the magnetic thermometer over the range 1.5–25 mK. A second cycle was then used to cool the lower stage to 1.5 mK where the measurements were started.

Ideally, the  $^3\text{He}$  level needed 20–30 hours to settle; however, the routine filling of the main helium dewar every 36 hours was disruptive to the level and therefore a complete measurement was made within this interval. The measurement consisted of three stages: The level was allowed to settle for  $\sim 8$  hours, heat was added above the porous plug for 8–10 hours, and finally the heat was switched off. Throughout the interval, the level was monitored, indicating the initial approach to equilibrium, the approach to the level difference generated by the added heat, and the final approach to equilibrium. In all cases the final levels had to be established by extrapolation. Each level change was small and consequently it was difficult to determine both the final level and time constant with any accuracy. Therefore during one of the intervals between helium fills a large level change was induced and allowed to decay; this fixed the time constant which is temperature independent up to 20 mK. Each final level was then determined by making several fits of small sections of each level versus time curve to an exponential decay differential equation with the time constant fixed, and averaging. Thermal equilibrium was not a problem; the magnetic thermometer time constant was  $\sim 10$  minutes.

The result of the experiment itself was a tabulation of  $\Delta T$  and  $\Delta H$  for the particular heat input  $\dot{Q}$  used at temperature  $T$ , for a set of temperatures from 1.5 mK to 20 mK. The  $^3\text{He}$  level difference,  $\Delta H$ , was converted to  $\Delta P$  by correcting for the small level change above the plug (see Fig. 1) where the cross-section was  $20\times$  larger than that within the capacitor and then multiplying by the usual  $\rho g$ .

### III. RESULTS AND ANALYSIS

The thermal resistance,  $R = \Delta T/\dot{Q}$ , is shown as a function of temperature in Fig. 2. It has a temperature dependence that reflects the dominance of boundary scattering of the  $^3\text{He}$  quasiparticles at low temperature and of scattering by other quasiparticles at high temperature. An analysis of these measurements must take into account the thermal resistance of the  $^3\text{He}$  in the porous plug, where scattering is by both boundaries and other quasiparticles and the thermal resistance of the bulk  $^3\text{He}$  above and below the plug, where boundary scattering can be neglected. Within Fermi liquid theory, the thermal conductivity of liquid  $^3\text{He}$  is given by [9]

$$\kappa = \frac{1}{3} C v_F \ell \quad (9)$$

where  $C \propto T$  is the heat capacity per unit volume,  $v_F$  is the Fermi velocity, and  $\ell$  is the  $^3\text{He}$  quasiparticle mean

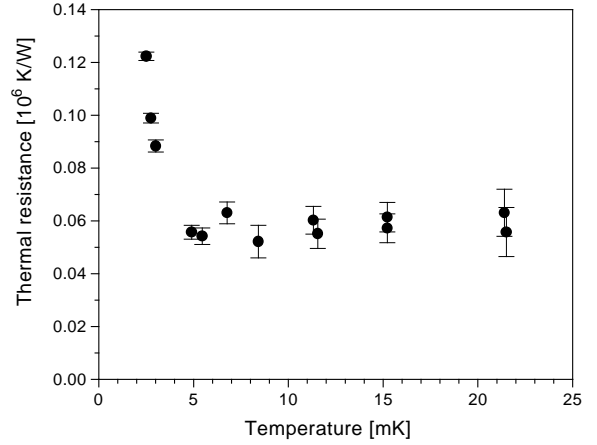


FIG. 2. The measured thermal resistance of the liquid  $^3\text{He}$  between the thin film heater and the  $^3\text{He}$  reservoir.

free path. In the bulk  $\ell = \ell_q \propto T^{-2}$ , the mean free path due to scattering by other quasiparticles. In the plug, in the usual way with two scattering processes,  $\ell = \ell_q d / (\ell_q + d)$  where  $d$  is the pore diameter. Therefore the total thermal resistance is

$$R = R_{\text{plug}} + R_{\text{bulk}} \quad (10)$$

$$= \left( \frac{L}{\kappa A} \right)_{\text{plug}} + \left( \frac{L}{\kappa A} \right)_{\text{bulk}} \quad (11)$$

$$= \alpha' T \left( 1 + \frac{\ell_q}{d} \right) + \alpha'' T \quad (12)$$

$$= \alpha T + \beta / T \quad (13)$$

where  $\alpha'$ ,  $\alpha''$ ,  $\alpha$  and  $\beta$  are constants. That is, we expect  $RT = \alpha T^2 + \beta$ .

Fig. 3 is a plot of  $RT$  versus  $T^2$  for the present results (closed circles, left scale) and for the earlier pure  $^3\text{He}$  results (open circles, right scale). The  $RT$  axes have the same scale factor but have a relative shift; this was done to show that within the experimental uncertainty there is a change in the intercept (the boundary scattering term in the plug) but not to the slope (the quasiparticle-quasiparticle term in the plug and in the bulk). The solid line fit to the results is not in fact a straight line. Anderson et al. [44] and Greywall [45] have measured the thermal conductivity of bulk  $^3\text{He}$  and found corrections to the first order result,  $\kappa \propto T^{-1}$ . We have used Greywall's result,  $\kappa = 2.91 \times 10^{-4} (T - 12.2T^2 + 74.4T^3)^{-1} \text{ W m}^{-1} \text{ K}^{-1}$  with  $T$  in kelvin.

The intercepts are given by  $RT = 240 \pm 20$  and  $320 \pm 20 \text{ K}^2/\text{W}$  for the four  $^4\text{He}$  monolayer and pure  $^3\text{He}$  measurements respectively, a drop of 25% on pre-plating. By using equation (9) and an effective area calculated with the model of Robertson et al. [46], the effective pore diameters were calculated to be  $36 \pm 11$  and  $27 \pm 8 \text{ nm}$  respectively.

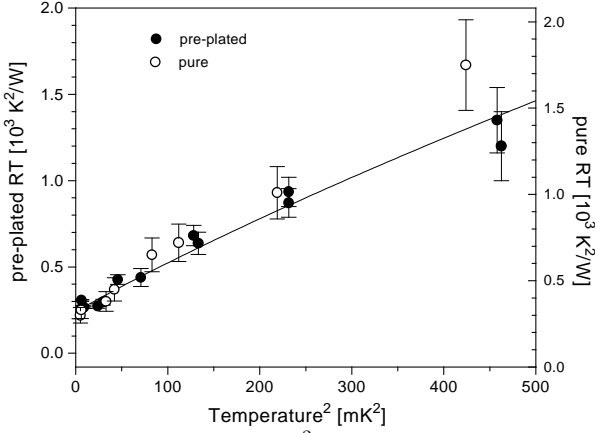


FIG. 3. Graph of  $RT$  vs.  $T^2$  where  $R$  is the measured thermal resistance. The closed circles (left scale) are the new results for the  $^4\text{He}$ -plated plug. The open circles (right, shifted scale) are the earlier pure  $^3\text{He}$  results. The fitted line is discussed in the text.

The time constant for mechanical equilibrium of the  $^3\text{He}$  through the porous plug was  $7.0 \pm 0.1$  hours. This was a similar 30% reduction from the 10 hour time constant for the pure  $^3\text{He}$  experiment. The pore diameter can be estimated from these time constants. Again we follow Robertson et al. in assuming an intersecting cylinder model for the pores. The volume flow rate along a cylinder of diameter  $d$  and length  $L$ , assuming diffuse scattering at the cylinder walls, is [9]

$$\frac{dV}{dt} = \frac{\pi d^3 \Delta P}{4nm^*v_F L} \quad (14)$$

where  $n$  and  $m^*$  are the number density and effective mass of the  $^3\text{He}$  quasiparticles and  $\Delta P$  is the pressure difference between the ends. For a  $(35 \pm 3)\%$  packing fraction, the intersecting pore model gives the following relation between the number of cylinders in the flow direction and the cylinder diameter:  $N\pi d^2/4 = (0.40 \pm 0.08)A$  where  $A$  is the cross-section of the plug. A straightforward mechanics calculation of the time constant then yields  $d = 43 \pm 9$  and  $30 \pm 7$  nm for the cylinder (pore) diameters for the four  $^4\text{He}$  monolayer and pure  $^3\text{He}$  measurements respectively.

Table I brings together the results from the two different measurements on the two  $^3\text{He}$  samples. Also included are the diameters deduced from the Knudsen flow of  $^4\text{He}$  gas through the plug at room temperature and from the viscous flow of pure liquid  $^3\text{He}$  at 500 mK, where  $\ell_q \ll d$  [1]. The first conclusion to be drawn is that the estimates based upon boundary scattering are significantly smaller than the diameter deduced from the surface area of the porous plug. Therefore the intersecting cylinder model is not appropriate for the packed powder despite giving a good description of sintered metal powder. The results suggest that a large fraction of the boundary scattering is in the backward direction, so decreasing the mass

TABLE I. The effective pore diameter of the porous plug determined by different methods. The liquid  $^3\text{He}$  fluid flow was performed below 20 mK in the boundary scattering regime. The  $^4\text{He}$  gas measurement was made at room temperature; the mean free path was  $\sim 300$  nm. The heat flow measurements were derived from the low temperature limit of the thermal resistance. Viscous flow measurements were performed at 500 mK where  $\ell_q \ll d$ . In all cases the Robertson et al. model was used to describe the porous structure and accounted for most of the uncertainty.

Experiment	Pore Diameter (nm)		
	90 $\pm$ 8		
	Liquid $^3\text{He}$		$^4\text{He}$ Gas
	Pure	$^4\text{He}$ -Plated	
Fluid Flow (Knudsen)	30 $\pm$ 7	43 $\pm$ 9	40 $\pm$ 8
Heat Flow	27 $\pm$ 8	36 $\pm$ 11	
Viscous Flow (500 mK)	80 $\pm$ 20		

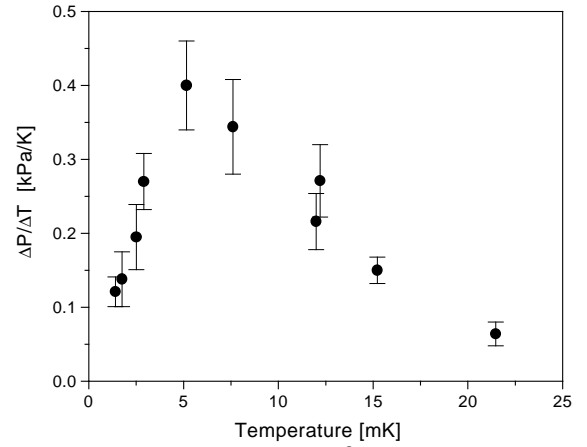


FIG. 4. The measured liquid  $^3\text{He}$  thermomechanical coefficient for the  $^4\text{He}$ -plated porous plug.

and heat flows. This may be reasonable given that all surfaces are convex within a packed powder whereas the formation of necks by the sintering process will give rise to both convex and concave surfaces in a sintered metal powder. The second conclusion is that the calculated diameters are larger for the  $^4\text{He}$ -coated and presumably specular surfaces. However, without a good model for the structure, it is not possible to relate the measured pore diameters to a specularity parameter.

Fig. 4 shows the measured thermomechanical coefficient as a function of temperature. This coefficient is a blended combination of two separate coefficients  $(\Delta P/\Delta T)_{\text{bd}}$  and  $(\Delta P/\Delta T)_{\text{qp}}$  arising from scattering of the quasiparticles by boundaries and other quasiparticles respectively. We follow the Nordheim-Gorter approach to the thermoelectric power resulting from two or more separate scattering processes and write,

$$\left(\frac{\Delta P}{\Delta T}\right)_{\text{meas.}} = \frac{(\frac{\Delta P}{\Delta T})_{\text{bd}} R_{\text{bd}} + (\frac{\Delta P}{\Delta T})_{\text{qp}} R_{\text{qp}}}{R_{\text{bd}} + R_{\text{qp}}} \quad (15)$$

where  $R_{\text{bd}}$  is the thermal resistance due to boundary

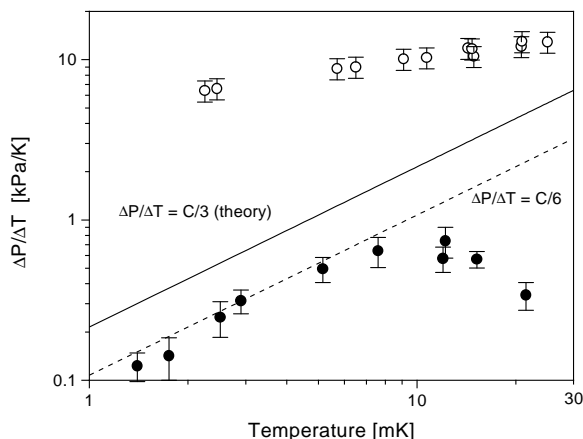


FIG. 5. A log-log plot of the derived boundary-scattering liquid  $^3\text{He}$  thermomechanical coefficient for the  $^4\text{He}$ -plated porous plug (closed circles) as a function of temperature. Also shown are the earlier pure  $^3\text{He}$  results (open circles) and the theoretical result from Edwards et al. (solid line). The dashed curve is discussed in the text.

scattering alone and  $R_{\text{qp}}$  is due to quasiparticle scattering alone. We know that  $(\Delta P/\Delta T)_{\text{qp}} = 0$ , within experimental error [1]. Furthermore the measured thermal resistance has been separated as shown in Fig. 3. The derived  $(\Delta P/\Delta T)_{\text{bd}}$  is shown as solid circles in Fig. 5, again as a function of temperature. A log-log format was chosen so that the present results could be compared with the earlier work on pure  $^3\text{He}$  (open circles) and the theoretical calculation of Edwards et al. [10] (solid line).

Clearly, the  $^4\text{He}$  pre-plating had a striking effect on the thermomechanical coefficient, reducing it by up to  $30\times$  at 2 mK. This is to be compared to the  $\sim 30\%$  effect on the thermal and flow conductivities in the low temperature limit of boundary scattering. Other features to be brought out are as follows: The coefficient is linear in temperature, within experimental error, in the low temperature limit, as predicted by the theoretical calculation and as expected from the analogy with diffusion thermoelectricity. However, the results seem to follow  $(\Delta P/\Delta T)_{\text{bd}} \sim s/6v$ , the dashed line, rather than the theoretical  $s/3v$ . The reason for this disagreement is not known; the theoretical result is independent of whether the geometry is that of cylinders or a model porous system and even of whether the boundary scattering is elastic or inelastic [10]. Another aspect of the results that is puzzling is that the coefficient is linear in temperature only in the low temperature limit where  $d \ll \ell_q$ ; either the boundary scattering thermomechanical coefficient decreases with increase in temperature or the Nordheim-Gorter procedure is not applicable in the region where  $d \gtrsim \ell_q$ . Even 20 mK is well below the Fermi temperature and so it is unlikely that the coefficient would decrease. The Nordheim-Gorter procedure, which was designed to deal with two or more impurity types, may not be appropriate to describe the transition from the Knudsen limit to the hydrodynamic limit. This

is perhaps a theoretical challenge.

The most intriguing result is that in the original experiment with pure  $^3\text{He}$  the thermomechanical coefficient was an order of magnitude larger than with the pre-plated surface, and the temperature dependence was  $\sim T^{0.3}$  even in our low temperature limit. Similar behaviour has been seen in thermoelectricity: Dilute alloys of noble metals with transition metal solutes have shown giant thermopowers with non-linear temperature dependence [47,11]. These have since been attributed to the Kondo effect and other magnetic effects in these dilute magnetic alloys [12]. The switching off of the ‘giant’ thermomechanical coefficient by replacing the magnetic  $^3\text{He}$  surface atoms with non-magnetic  $^4\text{He}$  surface atoms is convincing evidence for the magnetic origin of the enhancement. Further support comes from an entropy calculation. The thermomechanical coefficient depends upon the entropy, as does the thermoelectric power in a metal [11] and the phonon thermomechanical effect [2]. In the confined geometry of the porous plug the surface  $^3\text{He}$  atoms contribute a large fraction of the total entropy. If we postulate that there are 18 atoms/nm<sup>2</sup> in the first two layers, an entropy of  $k_B \ln 2$  per atom and use our measured surface area (1.2 m<sup>2</sup>) and pore volume ( $2.5 \times 10^{-8}$  m<sup>3</sup>), then  $S \sim 200 \mu\text{J/K}$  or  $s/v \sim 8 \text{ kJ/Km}^3$  or  $\Delta P/\Delta T \sim 8 \text{ kPa/K}$ . This calculation shows that the degrees of freedom do exist in the magnetic solid layers to account for a large thermomechanical coefficient. Measurements of the heat capacity of the solid  $^3\text{He}$  magnetic layers on the surface of sintered silver powder [29] and vycor glass [30] show a heat capacity of  $\sim 15 \mu\text{J/Km}^2$  from 1 to 20 mK and diminishing beyond 20 mK. This heat capacity has been attributed to a wide range of Weiss temperatures on the inhomogeneous surfaces. It would modify the entropy calculation, dropping it by about 25% at 2 mK and by a diminishing fraction as temperature is increased. This could explain the weak temperature dependence of the thermomechanical effect with pure  $^3\text{He}$ .

#### IV. CONCLUSIONS

The addition of four monolayers of  $^4\text{He}$  to the surface of the porous plug lowered the thermomechanical coefficient due to boundary scattering by up to a factor 30 to a low temperature limiting value of  $\Delta P/\Delta T = (100 \pm 15)T \text{ kPa/K} \sim s/6v$ , with  $T$  in kelvin. This is half the theoretical result, a disagreement for which we have no explanation. Looking back to the original pure  $^3\text{He}$  result, it was clearly anomalously high and reminiscent of the giant thermopowers in dilute magnetic alloys. The dramatic effect of adding the non-magnetic  $^4\text{He}$  monolayers is evidence that the enhancement was due to magnetic scattering by the solid-like Curie-Weiss magnetic  $^3\text{He}$  monolayers at the interface. The nature of the scattering is not clear. From the discussion in the Introduction we

know that scattering of the quasiparticles by the magnetic  $^3\text{He}$  layers is diffuse. However, replacing the  $^3\text{He}$  by  $^4\text{He}$  at the interface changes the scattering to specular, signifying that, on the length scale  $\sim 2\pi/k_F$ , the scattering surfaces must be geometrically flat. It is also known that both spin-flip and energy exchange, during boundary scattering of the  $^3\text{He}$  quasiparticles, have a very low probability ( $\sim 10^{-8}$ ) even for pure  $^3\text{He}$ ; therefore the scattering is close to elastic in the usual sense. The only possibility is to suppose that the pure  $^3\text{He}$  interface appears magnetically rough to the  $^3\text{He}$  quasiparticles.

Within experimental error the measurements of fluid flow and heat flow through the porous plug were consistent and gave effective pore diameters of  $\sim 40$  nm for the  $^4\text{He}$  pre-plated surface and  $\sim 30$  nm for the pure  $^3\text{He}$  case. The comparison is evidence for increased specularly for the  $^4\text{He}$ -plated surface. However, since both effective pore diameters are well below the 90 nm deduced from the surface area of the plug, there is need for a better model to describe transport in the pressed powder plug. As discussed above, probably a large fraction of the  $^3\text{He}$  quasiparticle scattering was back-scattering.

From the above conclusions, we can see a clear need for more experiments. A more ideal geometry is needed to confine the  $^3\text{He}$ . The Anopore material [48] used for helium studies by Hallock's group [49] looks very promising; it has parallel non-intersecting cylindrical pores with a high porosity. At the same time, the technique needs to be revised to reduce the 7–10 hour time constant to achieve equilibrium. Nevertheless, the giant thermomechanical effect has been demonstrated and remains to be understood in terms of scattering by the magnetically rough interface.

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\* harrisjp@physics.queensu.ca; physics.queensu.ca/lowtemp/

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